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TITLE: MECHANICAL PROPERTIES, SOLUBILITIES, AND PROCESSABILITIES IN
THE DESIGN OF THE FIRST SUPER-STRONG LIQUID-CRYSTALLINE
POLYMERS

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MECHANICAL PROPERTIES, SOLUBILITIES, AND PROCESSABILITIES IN THE DESIGN OF THE FIRST SUPER-STRONG LIQUID-CRYSTAL POLYMERS

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Introduction:

Solidified super-strong (SS) liquid-crystalline polymers (LCPs) are designed to be the first polymers to have good compressive strengths, as well as to have tensile strengths and tensile moduli significantly greater than existing strong LCPs (i.e., backbone LCPs, such as Kevlar). These SS LCPs have also been designed with certain features to give good solubilities and processabilities.

SS LCPs are a class of specially-designed combined LCPs in which the backbones align with other backbones while the side chains of different molecules align with each other in interdigitated structures, leading to three-dimensional (3D) LC ordering of the molecules. The side chains pack more or less perpendicularly to the backbones. See Fig. 1.

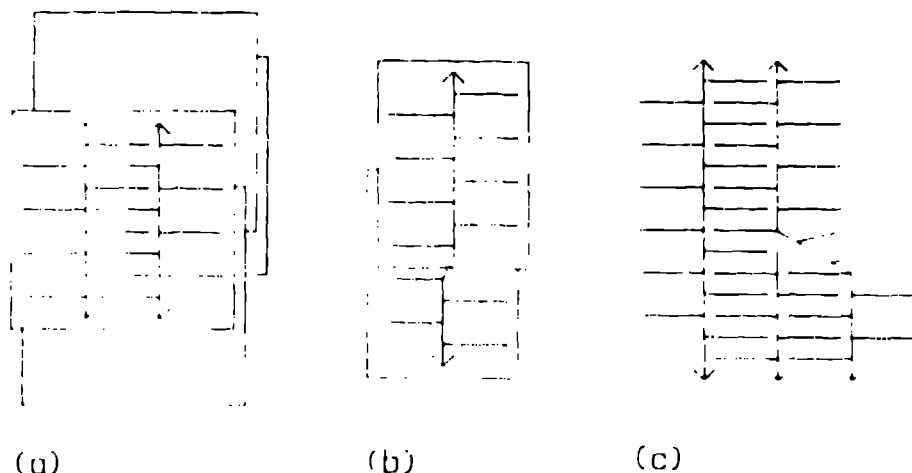


FIGURE 1. Schematic diagrams for SS LCPs illustrating (a) the tendency of the backbones and side chains to pack in a plane, and the orientational alignment of these planes, such that the backbones in one plane align with backbones in other planes and similarly for side chains; (b) sub-molecular strips of a molecule packing in adjacent parallel planes; and (c) side-chain interdigitation with several different molecules in different sub-molecular strips. [The lines represent the long axes of the parts of the molecules, where these parts can have both rigid and semiflexible sections. The arrows indicate the continuation of the backbones.]

As seen in Figs. 1(b)-1(c), small naturally-occurring

defects in the packing of the backbones and side chains of the SS LCP molecules give rise to an effective long-range 3D LC ordering (thus, strength) in the system.

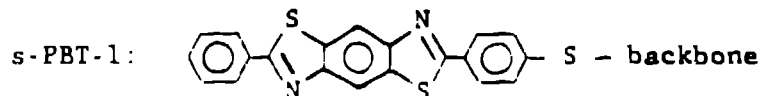
The key feature of this new class of LCPs is 3D exceptional strength on a microscopic, molecular level (thus, on a macroscopic level), in contrast to present LCPs (such as Kevlar) with their 1D exceptional strength. While existing strong LCPs are limited in technical applications primarily to fibers in woven fabrics and composite matrices, SS LCPs can be used to make fibers, films, and bulk materials from the pure SS LCP (as well as from the SS LCP in a composite matrix).

The theoretical prediction and design of the first SS LCPs was mentioned by this author in Ref. 1 and has been detailed by this author in Refs. 2, 3, and 4(a). The author has filed a patent application[5] on the details of the theoretical prediction and design of the first SS LCPs. SS LCPs were first proposed[6] and designed by this author in 1983. At the request of a related effort at Los Alamos to chemically synthesize some of these theoretically-designed SS LCPs, the author had delayed disclosure and publication (until recently) of the details of the theoretical prediction and design of the SS LCPs until the first syntheses were close to completion.

The prediction and design (atom by atom, bond by bond) of the molecule chemical structures of the first SS LCPs was accomplished using the theory presented by this author in Refs. 2 and 4 and earlier versions of this theory as presented by this author in other papers[1,7-13] dating back to 1983. The theory gives very good agreement (relative deviations between 0% and less than 6.2%) compared[2,4] with experiment for various thermodynamic and molecular ordering properties (including transition temperatures between various phases, orientational ordering, and radii of gyration) for existing backbone LCPs and side-chain LCPs, as well as trends[1,2,4,7-13] in various thermodynamic and molecular ordering properties as a function of pressure, temperature, and details of molecule chemical structure for various LC systems. There are no ad hoc or arbitrarily adjustable parameters in this theory.

Enhanced Mechanical Properties:

Table I shows the calculated increases in mechanical properties (tensile modulus, tensile strength, and compressive strength) for several theoretically-designed SS LCPs over these properties for the respective backbone LCPs.



The PBO-like side-chain s-PBO-1 is obtained by substituting -O- for each -S- in s-PBT-1.

The chemical syntheses of the theoretically-designed SS LCPs b-Kev-1 / s-Kev-1 [NH], b-Kev-1 / s-PBT-0, and b-Kev-1 / s-PBT-1 in Table I are nearing completion at Los Alamos. [14,15]

For some SS LCPs, the side chains of a molecule pack on alternating opposite sides of the backbone, as shown in Fig. 1. For the SS LCPs in Table I, the side chains of a molecule pack on the same side of the backbone.

The better the processing of the LCP, then the closer one comes to achieving the increases in mechanical properties shown in Table I.

The increases in tensile strength and compressive strength for the SS LCPs in Table I are the same, since these increases involve the work done when an interdigitated side chain is moved away from a second side chain and closer to a third side chain--up to the point of repulsion of the first side chain out of the plane of packing, thus causing physical failure of the sample. (Here, the first side chain starts out interdigitated between the second side chain and the third side chain.) This work is the same under tension as under compression. See Fig. 1(a).

For comparison, here are the experimental ranges[16] of values of mechanical properties for the backbone LCPs Kevlar, PBT, and PBO: 130 to 365 GPa for tensile modulus, 3.5 to 5.8 GPa for tensile strength, and 0.40 to 0.48 GPa for compressive strength. Kevlar is the same as b-Kev-1 without a side chain (s-...); PBO is the same as b-PBO without a side chain (s-...); and PBT is the same as PBO, except every -O- in PBO has been replaced by -S- in PBT.

The calculated increases in mechanical properties for SS LCPs are about 2 to 25 times the reported experimental mechanical properties for the backbone LCPs, with the largest increases occurring (as expected) in the compressive strength. It has been estimated (see Ref. 16) that the experimental values for the backbone LCPs could be doubled with maximized processing. Even with maximized processing of existing backbone LCPs, the SS LCPs are still calculated to have significantly enhanced mechanical properties.

The calculated increases for mechanical properties for

SS LCPs in Table I are consistent with the calculated enhanced LC orientational and positional ordering of these SS LCPs, as presented elsewhere[3,4(a)] by this author.

Enhanced Solubilities:

The side chains in the SS LCPs greatly improve the solubility of the backbones. The side chains are predicted to be soluble in most of the same common tractable solvents in which monomeric LC molecules are soluble. The solubility of the side chains in these solvents thus increases the solubility of the whole molecule (including the backbone) in these solvents. That is, the side chains help pull the backbones into solution.

Enhanced Processabilities:

Each side chain in SS LCPs is connected to the backbone via a partially flexible joint that is, via a small functional chemical group (such as -O-, -S-, -NH-, -CH₂-) that is connected by only a single bond to the backbone and by only a single bond to the rest of the side chain. The small size of this group and the semiflexibility of these single-bond connections will allow the side chain to be fold down somewhat--with minimum steric hindrance--parallel to the backbone (after the manner of spokes or ribs of an umbrella) when linear processing (such as flow through a pipe) of the SS LCP is required. See Fig. 2.

After linear processing is completed, the side chains can be then be folded back out from the backbone so as to pack more or less perpendicularly to the backbone such that the LCP molecules align in the three dimensions (i.e., backbones align parallel to one dimension and the side chains align in the other two dimensions) as required for super-strong mechanical properties. See Fig. 1(a). Fig. 2 is a higher energy state than Fig. 1(a).



FIGURE 2. Schematic diagram showing the side chains folded down somewhat in linear processing.

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